Anthropogenic Impacts on the Atmosphere

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Occurrence and Gas-Particle Partitioning of Organic UV Filters in Urban Air

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KEYWORDS

Organic UV-filters, active air sampling, gas-particle partitioning, seasonal variations

ABSTRACT

A retrospective analysis of a comprehensive series of high volume air samples (n=70) collected during 2010-2011 in Toronto (Canada) was performed. Seven UV compounds were analyzed by GC-MS/MS with sum of concentrations (gas + particle phase) ranging from 80-2030 pg/m^3. Homosalate (HMS) was the most prevalent organic UV-filter in air (47% of the total concentration), followed by 2-ethylhexyl salicylate (EHS, ~29%), E- and Z-2-ethylhexyl 4-methoxycinnamate (EHMC, ~17%). Ambient air (gas+particle phase) concentrations of organic UV-filters showed a strong seasonality, with peak levels during the summer. An analysis of Clausius-Clapeyron slopes indicated that much of the ambient burden of organic UV-filters is explained by volatilization from terrestrial and aquatic surfaces and supplemented with human activities and use of lotions and sunscreens, containing organic UV-filters, in addition to the its use in plastics, textiles, paints and pesticides. The results showed that organic UV-filters exist mainly in the gas phase with some exceptions. For instance, octocrylene (OCR), which was associated with both gas and particle phases, and avobenzone (AVB), which was predominantly in the particle phase. Lastly, this study revealed the need for basic physical chemical property data for organic UV-filters, including information on transformation rates and products, for better evaluating their environmental fate and effects.

INTRODUCTION

Organic chemicals used in sunscreens and other ultraviolet (UV) protection applications are gaining attention as emerging pollutants. These chemicals are used mainly in personal care products such as lotions, sunscreens and cosmetics to protect skin from dangerous UV radiation, as well as in protective coatings (e.g. paints and polymers) to prevent the degradation of these

materials.[1] As a result, these chemicals may be introduced into the environment during their production, usage and disposal. They are released to air by evaporation during use of products containing them (e.g., sunscreen lotions) or during wastewater treatment .[2,3]

Several organic UV-filters have shown estrogenic activity,[4–8] tendency to accumulate in aquatic organisms and have been detected at various trophic levels.[9] Evidence suggesting bioaccumulation [10] and biomagnification in marine organisms has been found.[11,12] Organic UV-filters could also be involved in DNA damage in corals and coral bleaching by promoting viral infection.[13,14]The occurrence of organic UV-filters in the Arctic environment indicates that they have sufficient transport potential and environmental persistence to be of concern.[15] The presence of organic UV-filters in indoor air and dust has also been demonstrated, where it poses a concern for human exposure.[16–20]

To date, several of studies have considered the environmental occurrence of organic UV-filters in a wide variety of environmental compartments such as sediment,[21–24]water,[9,25–27]fish,[28–31]beach sand [32,33] and coral communities.[34]More recently, the presence of organic UV-filters has been reported in the air near coastal areas using biomonitors[35] and at wastewater treatment plants using passive air sampling.[36]However, no information has been reported concerning the presence of organic UV-filters in ambient air using active air sampling, or gas-particle partitioning of these emerging pollutants. In fact, the atmospheric fate of organic UV-filters is relatively unknown. Recent assessment of their physical and chemical properties suggests that organic UV-filters are relatively persistent in air and are semi-volatile compounds, that should exist both in the gas-phase and associated with particles.[37]

To address these data gaps related to organic UV-filters and their occurrence in air, we performed retrospective analysis of a comprehensive set of high volume air samples (n=70)

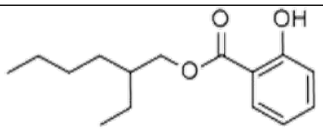
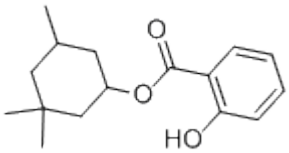
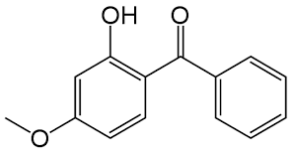
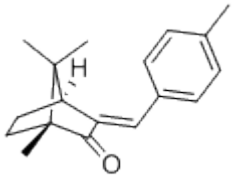
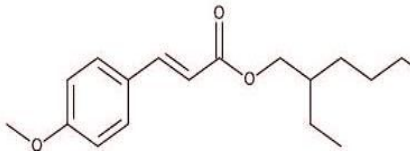
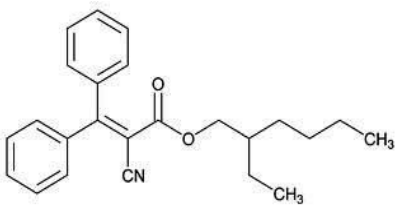
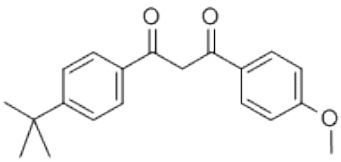
collected over several months during 2010-2011 in Toronto, Canada. These samples were previously analyzed for a range of compounds including siloxanes, flame retardants (FRs), per- and polyfluoroalkyl substances (PFASs), among others.[38–40] The retrospective analysis for the organic UV filters was triggered by a growing body of research showing the environmental relevance of these compounds and a lack of information on their levels and partitioning in air. This new information will improve our understanding of the atmospheric fate pathways of organic UV-filters and will have implications for future risk assessments.

MATERIALS AND METHODS

Chemicals

The list of organic UV-filters and their structures targeted this study are shown in Table 1.The target analytes, which included 2-ethylhexyl salicylate (EHS, 98%), homosalate (HMS, 98%), benzophenone-3 (BP-3, 98%), 3-(4-methylbenzylidene)camphor (4-MBC, 98%), 2-ethylhexyl 4-methoxycinnamate (EHMC, 98%), octocrylene (OCR, 98%) and avobenzone (AVB, 98%),were supplied by Sigma Aldrich Oakville, ON, Canada. In addition, one mass-labelled internal standard was used (i.e. d10-benzophenone 98% from CDN Isotopes Inc., Pointe-Claire, Quebec, Canada).

87 **Table 1.** Structures and selected property information for UV compounds.

UV-Filter	Chemical Structure	Molecular formula	MW	K_{OA}	P_L/Pa x 10^{-2} (at T/K = 298)	Maximum concentration[a] (%)
2-Ethylhexyl salicylate (EHS)		$C_{15}H_{22}O_3$	250.3	8.8[b]	0.6[b]	5
Homosalate (HMS)		$C_{16}H_{22}O3$	262.3	9.3[b]	1.1[d]	15
Benzophenone-3 (BP-3)		$C_{14}H_{12}O_3$	228.2	10[b]	0.5[d]	6
3-(4-Methylbenzylidene)camphor (4-MBC)		$C_{18}H_{22}O_3$	254.4	10[b]	1.8[d]	6
2-Ethylhexyl 4-methoxycinnamate (EHMC)		$C_{18}H_{26}O_3$	290.4	9.9[b] (9.7 (E), 9.1 (Z))[c]	0.02 (E)[c,e] 0.1 (Z)[c]	7.5
Octocrylene (OCR)		$C_{24}H_{27}NO_2$	361.5	13.8[b]	0.002[b]	10
Avobenzone (AVB)		$C_{20}H_{22}O_3$	310.4	12.6[b]	0.07[b]	3

[a]Maximum concentrations of Drug Medicinal Ingredients in Sunscreens ("Guidance Document Sunscreen Monograph", Health Canada, 2012); [b]EPA EPI suite; [c]Pegoraro et al.[37]; [d]Okeme et al.[41]; [e]Pegoraro et al.[42] MW=molecular weight, K_{OA}= octanol-air partition coefficient, E=trans isomer, Z=cis isomer.

Sampling and analysis

Sampling was carried out at the Environment and Climate Change Canada field station located in north Toronto (43°46′N, 79°28′W), approximately 18 km from the Lake Ontario shoreline. The station is surrounded by a mix of light industrial, light residential/commercial and some parklands. High volume active air samples (*n*=70) were collected using PS-1 type samplers (Tisch Environmental, Cleves, OH, USA) from March, 2010 to April, 2011. Approximately 330 m^3 of air was collected during each 24 h sampling period. The sampling device consisted of a glass-fiber filter (GFF) (Type A/E Glass, 102 mm diameter, Pall Corporation) for collecting the particle-phase followed by a Polyurethane Foam (PUF)/XAD–2 cartridge, for trapping the gas-phase compounds. This comprised 15 g of XAD–2 resin (Supelpak^{TM}–2, precleaned, Supleco Bellefonte, PA) sandwiched between a PUF plug (76 mm diameter and 60 mm thick, precleaned, Supelco, Bellefonte, PA) that was cut in half (i.e. 30 mm of PUF on either side of XAD-2 resin). Field blanks were collected periodically and involved inserting the sampling media into the high volume sampler, turning on the pump for a few seconds and then collecting the data in the same manner as real samples. All samples were stored at −20 °C until extraction within four weeks. The sample collection schedule and related details are reported in Table S1 of the Supporting Information (SI).

Extraction

The individual PUF/XAD–2 sandwiches and GFFs for each sample were Soxhlet extracted with petroleum ether/acetone (85/15, v/v) for ~6 h. The GFFs were extracted by sonication – three times with dichloromethane. All extracts were concentrated by rotary evaporation followed by gentle nitrogen blow-down to 0.5–1 mL in isooctane at which point 100 ng Mirex was added as the injection standard. The extracts were transferred to amber glass vials, sealed and archived in a freezer (-20 °C) for future retrospective analysis of emerging compounds. They were analyzed in 2015, i.e. four years after samples were extracted. Even though extracts were stored in the dark and at low temperature, there is no information about the stability of organic UV-filters extracts in organic solvents during years of storage. As a consequence, caution should be applied when interpreting the concentrations of UV-filters, because of the possibility that some of the compounds are degraded during storage. The organic UV-filters concentrations could therefore be underestimated. We think that this issue should be further addressed in future investigations, including the use of labelled standards for organic UV filters to check for losses.

Instrumental analysis

Analyses of organic UV-filters were performed retrospectively using archived extracts from the 2010 sampling campaign using a GC-MS/MS Agilent 7890B GC coupled with a 7000C Triple-Quad detector equipped with a 7693A autosampler (Agilent Technologies, Palo Alto, CA, U.S.). The MMI (multimode-inlet) splitless injector was maintained at 290 °C. The chromatographic separation was accomplished using two HP-5MS capillary columns (15 m × 250 μM, 0.25 μM) with back flush at the end of the run and research grade (>99.9999% purity) helium used as the carrier. The GC ramp conditions were as follows: 70 °C, hold 1 min; ramp at 15 °C/min to 300 °C; hold 2.0 min. Helium flows was set to 1mL/min and in constant flow mode. The injection was carried by using analyte protectants (APs)[43] and by pulsed pressure at 30 psi, hold for

0.5min and split (purge) time of 0.5min. The APs used were S and D sorbitol purchased from Sigma Aldrich Canada (1.2mg/mL in acetonitrile) in a 1 μL volume sandwich injection with the sample.

The transfer line temperature was set to 290 °C. Compounds were analyzed by MRM and electron ionization (70 eV). Both helium and nitrogen collision gases were set at 0.5 mL/min. The ion source temperature was maintained at 250 °C, and the temperature of both quadrupoles was maintained at 150 °C. Table S2 in SI provides information on the ionization mode, transitions, quantification and qualifier ions used for monitoring the target compounds.

Quality assurance/quality control (QA/QC)

Total method recovery was tested using a 50 μg/L solution of organic UV-filters spiked on polyurethane foam. Recoveries were between 90±5% for AVB and 150±11% for HMS (Table S3 in SI). Blank levels were assessed for 6 field blanks (PUF and GFF). For PUF blanks EHS and HMS showed the highest amounts (14 and 17 pg/m^3 respectively, based on 330 m^3 air volume), also these compounds were the most abundant in GFF blanks (0.24 and 0.25 pg/m^3 respectively). Method detection limits (MDL, pg/m^3) were calculated as the mean of the field blank values plus three standard deviations. The MDLs were calculated based on an average air volume of 330 m^3 resulting in concentrations in the range of 1.6-19 pg/m^3 for PUFs and 0.15-0.61 pg/m^3 for GFFs (for details see Table S4 in SI). If compounds were not detected in blanks, 1/2 of the instrument detection limits (IDLs) were used for calculating the MDLs. Instrument detection limits (IDLs) were calculated from the lowest standard, extrapolating to the corresponding amount of analyte that would generate a signal-to-noise ratio of 3:1. The IDLs ranged between 0.11-0.16 pg/μL for

153 EHS, BP-3, 4-MBC, OCR and AVB and 0.04-0.07 pg/µl for HMS and EHMC. Data reported in
154 this study is not blank corrected and only data above MDL are reported.

155 RESULTS AND DISCUSSION

156 **Concentrations in air of organic UV-filters**

157 The air concentrations of total organic UV-filters (gas + particle phase) ranged from 80 to 2030
158 pg/m^3 in the city of Toronto (Table 2 and Table S5 in SI). These concentrations were dominated
159 by HMS (26-960 pg/m^3) and EHS (20-580 pg/m^3), followed by the two isomers (Z+E) of EHMC
160 (24-300 pg/m^3). EHS and HMS were detected in almost 90% of the samples, while BP-3, Z-
161 EHMC and E-EHMC were detected at a rate of 70-78%. 4-MBC, OCR and AVB were only
162 detected in 35-56% of the samples. HMS was the most prevalent UV filter in air with a
163 contribution of 47% of the total concentration, followed by EHS(~29%),E- and Z-EHMC
164 (~17%), BP-3 and 4-MBC above 2%, while OCR and AVB represented less than 1% of the
165 total. This is in agreement with Shoeib et al. [36] who also reported a prevalence of HMS and EHS
166 in air at wastewater treatment plants (WWTPs) from Ontario, Canada. HMS and EHS levels in
167 air in the vicinity of urban WWTPs with secondary treatment (430-2450 and 320-1440 pg/m^3)
168 were similar to those reported in the present study (25-960 and 19-580 pg/m^3).

169 A correlation analysis between analyzed organic UV-filters showed a good correlation between
170 BP-3 and HMS ($r=0.89$, $p<0.05$), EHS and HMS ($r=0.76$, $p<0.05$) as well as between BP-3 and
171 HMS ($r=0.71$, $p<0.05$) (Table S6 in SI). The presence of these organic UV-filters in the
172 atmosphere could be associated with the use of sunscreen products and cosmetics containing
173 them but also with some pesticides, since repellent insecticides and some garden pesticides
174 contain these compounds[44]. Additionally, EHMC and BP-3 have been used as light stabilizers in

175 plastics,[45] while BP-3 is used in agricultural plastics films and paints as an UV absorber.[1]
176 Organic UV-filters could also be emitted to the atmosphere during the manufacture of products
177 containing these compounds. For example, during manufacture of plastic products the local
178 emission of each UV-stabilizer from a plastic processing site, assuming a production of 30 t/day,
179 was estimated to be 0.47 kg/day to wastewater and 0.15 kg/day to air.[46]

180 **Table 2.** Summary of UV-filter concentrations (pg/m^3) in air (gas and particle phases) and
181 regression parameters of ln P versus 1/T[a]
182

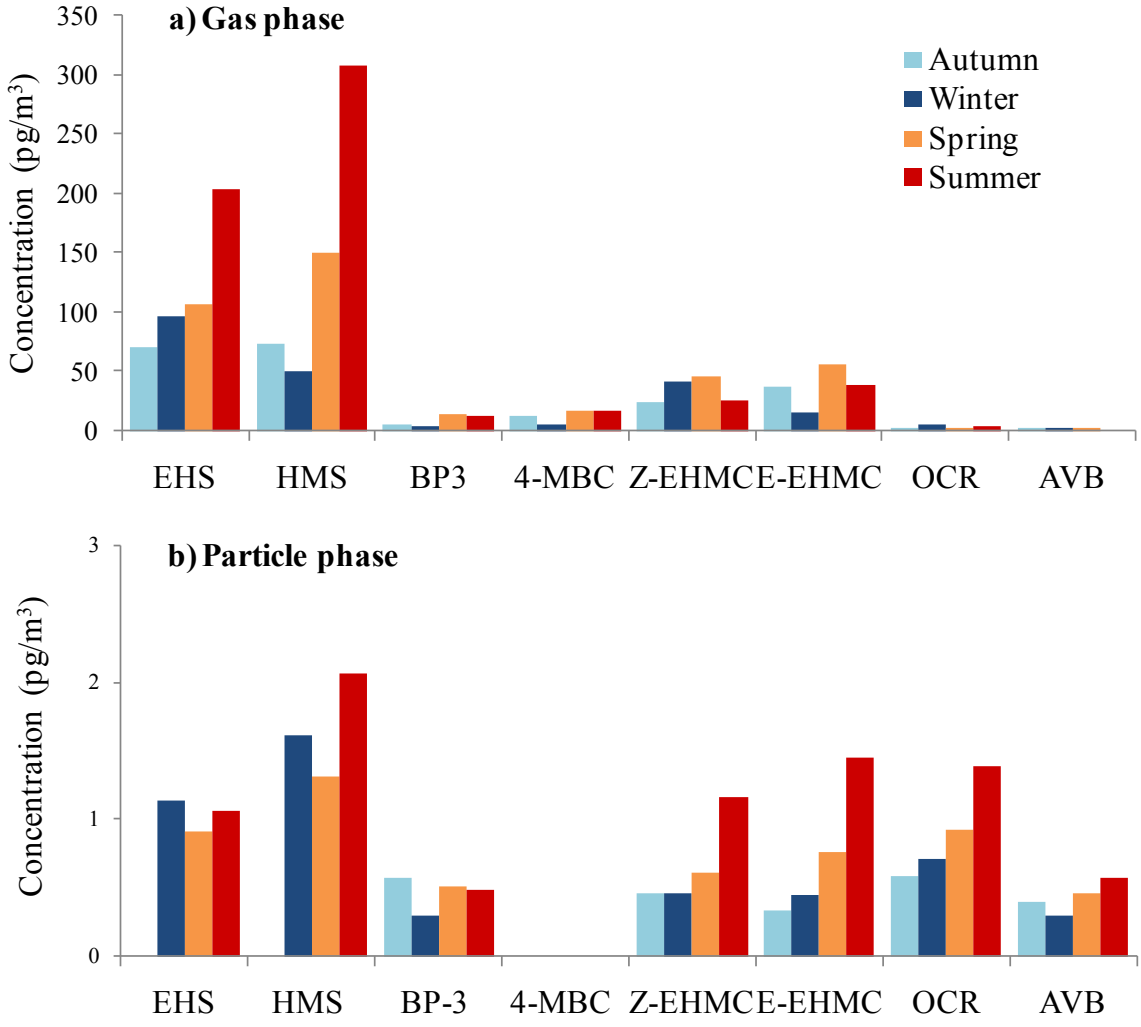
	Gas phase			Particle phase			Regression Parameters		
	Range	AM	GM	Range	AM	GM	Slope	r^2	Slope[b]
EHS	19-580	120	71	0.5-1.9	1.1	1.0	-4630±654	0.50	-
HMS	25-960	150	87	0.6-3.3	1.6	1.4	-5660±578	0.64	-
BP-3	3.8-58	12	8.7	0.2-1.1	0.5	0.4	-4510±881	0.56	-
4-MBC	4.4-47	15	12	0.4-1.0	0.5	0.5	-4360±621	0.67	-
Z-EHMC	12-90	40	33	0.2-12	1.0	0.5	-5710±1232	0.54	8540±61
E-EHMC	12-180	58	41	0.2-14	1.2	0.5	-5820±1850	0.40	9350±58
OCR	0.83-15	4.3	3.9	0.2-3.4	1.0	0.8	-1260±240	0.51	-
AVB	1.6-8.9	3.1	2.7	0.1-2.7	0.4	0.3	-918±1242	0.06	-

[a]Slope and regression coefficient r^2 for Clausius-Clapeyron plots; AM: arithmetic mean; GM: geometric mean; [b]Slope calculated by Pegoraro et al.[37] using the GC-RT method.

183

184 **Seasonal variations of organic UV-filters**

185 Seasonal variations of the total air UV-filter concentrations are shown in Figure 1. Monthly air
186 concentrations were calculated based on arithmetic mean concentrations of the weekly samples
187 (*n*=4 or 5 for each month) (Figures 2 and 3). Temperatures over the sampling period varied from
188 a monthly average of 26 °C in July to -5.9 °C in February.



189

Figure 1. Seasonal variations (March 2010 to April 2011) of the arithmetic mean concentrations of organic UV-filters in the gas (a) and particle (b) phases. Compounds with no bars were below MDL.

Most organic UV-filters both in gas (Figure 2) and particle phases (Figure 3) showed seasonal variations (e.g., higher concentrations in summer) suggesting direct input from emissions related to sunscreen usage combined with enhanced vaporization to air from other sources due to primary or secondary emissions (i.e., revolatilization). The same pattern for EHS and EHMC was reported in water for coastal environment by Sankoda et al.[47]. Sunscreens represent the major source of organic UV-filters in personal care products,[48] therefore being an important source during the warmer periods. Similarly, primary and secondary emissions to air from products that have been treated with UV filters or from previously deposited organic UV-filters is expected to increase at higher temperatures following a Clausius-Clapeyron type relationship. As the temperature rises, gas-phase air concentrations increase due to volatilization from surfaces such as soil, atmospheric particles, water, and also from products that have been treated with organic UV-filters. Vegetation could also be associated with secondary emissions and potentially (for some plant species) primary emissions of organic UV-filters. Measurements of biogenic volatile organic compounds produced by different desert plants concluded that EHS and HMS were emitted at significant rates.[49]These salicylic esters are predicted to be a protective mechanism of plants from UV radiation and the emission process would be driven by high ambient temperatures. Cottonwood (*Populus deltoides*), one of the species identified by Matsunaga et al.[49] as emitting EHS and HMS, is native to Ontario, suggesting an additional source of organic UV-filters to the air.

Seasonal variations of the gaseous organic UV-filters showed that the gas-phase concentrations of the more volatile compounds (EHS, HMS, BP-3 and 4-MBC) were significantly higher in the summer months compared to the winter months (ANOVA Friedman, $p<0.05$; Figure 1a). In the particle-bound fraction, Z-EHMC, E-EHMC and OCR showed higher concentrations in the warm season than the cold season (ANOVA Friedman, $p<0.05$), while AVB, EHS and HMS showed no clear seasonal pattern, maybe due to the low concentrations registered for these compounds, which were below to the detection limits in many cases (Figure 1b). Shoeib et al.[36] also found higher air concentrations of EHS, HMS, BP-3 and 4-MBC in summer compared to winter close to a wastewater treatment plant in an urban area. Similar seasonal variations were found for PFASs and FRs in the urban air of Toronto, Canada.[38,40]

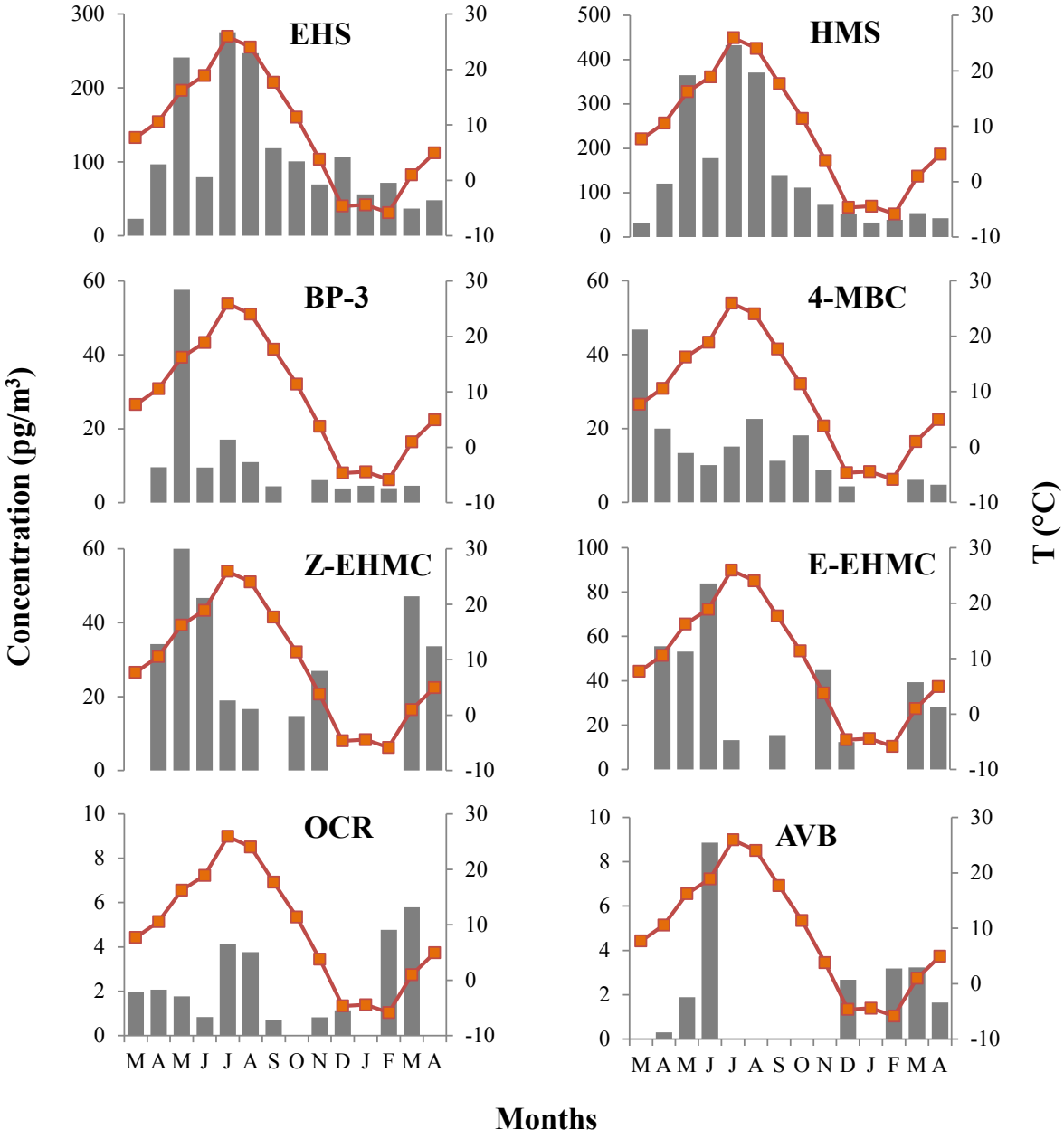


Figure 2. Seasonal variations (March 2010 to April 2011) of the arithmetic mean concentrations of organic UV- filters in the gas phase (grey bars) and average air temperature (orange line). Months with no bars were below MDL.

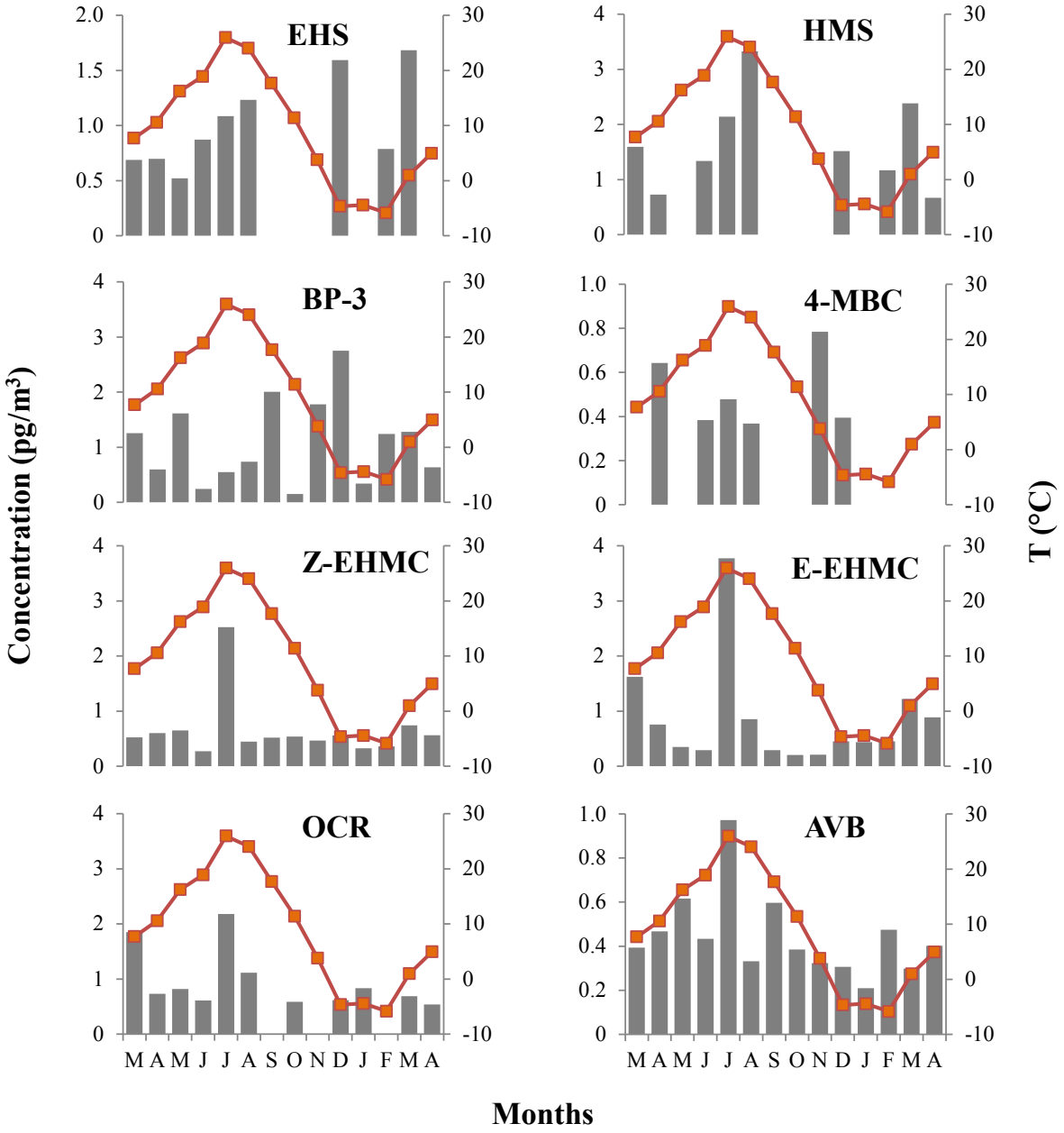


Figure 3. Seasonal variations (March 2010 to April 2011) of the arithmetic mean concentrations of organic UV-filters in the particle phase (grey bars) and average air temperature (orange line). Months with no bars were below MDL.

Effect of meteorological parameters

Seasonal variations in UV-filter concentrations are influenced by meteorological conditions, which play an important role in determining pollutant levels. Parameters such as temperature, wind speed, wind direction, rainfall and relative humidity have been reported to affect the air concentrations of semi-volatile organic compounds.[50,51]

Temperature

Partial pressure (atm) of individual compounds was calculated for each sample using gas-phase concentrations and the ideal gas law. As shown in Figure S1 in SI, for the majority of organic UV-filters (EHS, HMS, BP-3, 4-MBC, Z-EHMC and E-EHMC) air concentrations increased with air temperature, which results in a negative correlation between inverse temperature (1/T) and partial pressure (ln P) (Table 2). Steep slopes and high r^2 values for these Clausius-Clapeyron (C-C) plots indicate that temperature-controlled air–surface exchange and short-term transport influence the ambient gas-phase concentrations.[52,53]

The importance and nature of the contribution of surface-air exchange can be evaluated further by exploring the enthalpy of surface-air exchange (ΔH_{SA}, kJ/mol) derived from the slopes of the C-C plots in Figure S1 to enthalpy of phase change for vapor pressure, ΔH_{VAP} (representing volatilization to air from terrestrial surfaces) and the enthalpy of phase change for air-water exchange ΔH_{AW}, representing volatilization from water bodies (e.g., Lake Ontario, adjacent to Toronto)[54]. For Z- and E-EHMC, the derived ΔH_{SA} values were 47±10 and 48±15 kJ/mol, respectively, while values reported for ΔH_{vap} by Pegoraro et al.[37] were somewhat higher at 99 and 109 kJ/mol, respectively. Although, ΔH_{vap} are not currently available for the other organic UV-filters investigated here, it is reasonable to assume that values will not be too different than reported for the EHMC isomers. Values of ΔH_{AW} are typically lower than ΔH_{vap} for semi-

volatile organics[54] but have also not yet been reported for organic UV-filters. Based on the available information, the current analysis indicates that much of the ambient burden of organic UV-filters is explained by volatilization from terrestrial and aquatic surfaces, which is greatest in the summer, owing to increased usage of sunscreen lotions containing organic UV-filters during the warmer months.[55,56] There is a need for information on the physical and chemical properties of organic UV-filters as a function of temperature to better understand and predict their environmental fate and behavior in the atmosphere.

Wind speed, humidity and precipitation

Ambient air concentrations of organic UV-filters showed a general decreasing trend when the wind speed was >25 km/h. Multiple linear regression (MLR) analysis was performed to investigate the effect of temperature, wind speed and direction on gas-phase atmospheric concentrations of organic UV-filters (Table S7 in SI). Nevertheless, the relation between air concentrations and wind speed, rainfall or relative humidity was not statistically significant for any of the organic UV-filters. The addition of these parameters to the correlation showed no further contribution than the temperature itself. The lack of correlation between air concentration and wind speed could suggest that advection did not have a significant impact on the atmospheric concentrations measured in Toronto air. However, this interpretation is complicated by the need to consider wind direction and locations of potential sources relative to the sampling site. Currently there is insufficient information on sources and source regions that impacted the sampling. Wind speed also plays a role in enhancing surface-air exchange while at the same time higher wind speeds usually indicate a more unstable/turbulent and well-mixed atmosphere which could have the effect of diluting levels of organic UV-filters in air.[52] Atmospheric transformation

of UV filters is another process which could reduce concentrations, especially during the summer period when sunlight and oxidant levels are highest.[57]

Snowfall

Fourteen snowfall events were registered during the sampling period. For all UV- filters analyzed, total average concentrations (gas + particle phase) were 2-8 times lower during periods of high snowfall. Particularly, the amount of snowfall (in mm) was negatively correlated with the concentrations of EHS, HMS, Z-EHMC and E-EHMC, although, it was significant only for EHS ($p<0.05$, Figure S2 in SI). It is known that snowfall enhances the removal of organic chemicals from the atmosphere.[58] Nevertheless, more studies are needed to establish the process of wet deposition by rain and snow scavenging.

Gas-Particle Partitioning of organic UV-filters

The fraction of substance associated with the particle phase in air (ϕ) was calculated directly from measured data as the amount of chemical in the particle phase (C_p) divided by the total amount of chemical (particle phase + gas phase):

$$\phi=C_p/(C_{p+}C_g) \quad (1)$$

Partitioning of semi-volatile organic compounds between the gas and particle phases was parameterized using the gas/particle partition coefficient, K_p[59]:

$$K_p=(C_p/C_{TSP})/C_g \quad (2)$$

297 Where C_p and C_g are the organic UV-filters concentrations in the particle and gas phases (pg/m^3),
298 respectively, and C_{TSP} is the concentration of total suspended particles in the air ($\mu g/m^3$). The
299 predicted particulate percentages can be calculated using the equation:

300 $$\phi = K_p C_{TSP}/(1+K_p C_{TSP}) \quad (3)$$

301 K_p can be estimated from K_{OA} using a K_{OA}-based model[60]:

302 $$\text{Log } K_p = \log K_{OA} + \log f_{om} - 11.9 \quad (4)$$

303 Where f_{om} is the fraction of organic matter on the aerosol that is free to exchange chemical with
304 the air. Values of 0.1 and 0.2 were used for f_{om} to calculate K_p using the K_{OA} model because
305 these are typical values for urban air. Total suspended particulate matter (TSP) averaged
306 concentrations measured of 34±14 $\mu g/m^3$ [40]was used to calculate ϕ.

307 The distribution of organic UV-filters between the gas and the particle phases is presented in
308 Table 3. In general, higher temperatures favor volatilization of particle phase compounds into the
309 gas phase. Results revealed that UV-filter concentrations in the particle phase decreased from
310 winter to summer, suggesting a desorption process of these compounds from the particle phase
311 (Figure S3 in SI). The experimental data showed that most of the organic UV-filters are mainly
312 in the gas phase. The exceptions were OCR, which was associated with both gas and particle
313 phases, and AVB, which was predominantly in the particle phase.

314 Modeled and measured particulate percentages (Table 3) showed excellent agreement for most
315 compounds, except for OCR and AVB. Differences may be due to: i) uncertainties in the K_{OA}
316 predicted for these two organic UV-filters, ii) particles that may have passed through the particle
317 filter medium and/or iii) departure from equilibrium partitioning.

318 **Table 3.** Experimental (Exp) and calculated ($K_{OA\text{-}model}$) average of particulate percentage (ϕ/%)
319 using fraction of organic matter on the aerosol at 25 °C (f_{om}=0.1 and 0.2)

	ϕ (%)		
	Exp	$K_{OA\text{-}model}$	
		f_{om}=0.1	f_{om}=0.2
EHS	0.5±1.0	0.3	0.6
HMS	0.6±1.4	0.8	1.6
BP-3	5.3±4.6	4.0	8.1
4-MBC	0.2±0.7	3.8	7.8
Z-EHMC	1.3±4.1	0.5	1.1
E-EHMC	1.4±4.3	2.1	4.3
OCR	32±40	99.6	99.8
AVB	87±31	94.3	94.6

320

321 **Environmental implications and future work**

322 New information from this study provides insight to the sources, presence, partitioning, and
323 atmospheric fate pathways of organic UV-filters. The results demonstrate the important role of
324 human activities and secondary sources on ambient concentrations, especially during summer
325 months. This study highlights another class of chemicals that contributes to the chemical mixture
326 in air to which the environment and humans are exposed. Future studies should explore the
327 physical chemicals properties and toxicity of the organic UV-filters, including their
328 transformation products in air.[57,61,62] Future work should also investigate different source sectors
329 in urban air (e.g. traffic, industry, commercial, residential) to characterize primary emissions of
330 organic UV-filters.

ASSOCIATED CONTENT

Supporting Information

Additional details on sampling, meteorological data, organic UV-filters concentrations, statistical analysis, influence of meteorological conditions, seasonal variation, partitioning of organic UV-filters. This material is available free of charge via the Internet at http://pubs.acs.org.

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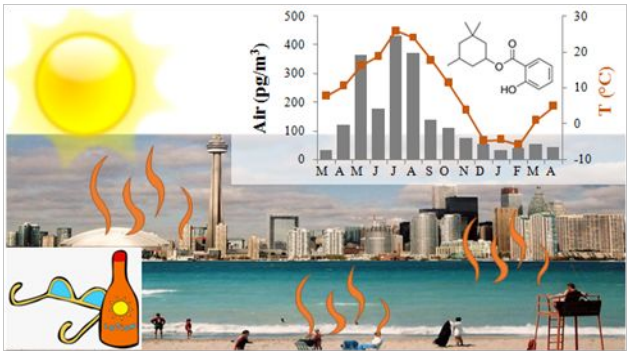

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